

Studies of Water-in-Oil Emulsions: Stability Studies

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Abstract

Studies to determine the stability of water-in-oil emulsions were conducted. Three oils were used to form emulsions and these were studied by rheological methods. It has been noted that the stability of emulsions can be grouped into three categories: stable, mesostable and unstable. The differences in the emulsion types are readily distinguished both by their rheological properties, and simply by appearance. The apparent viscosity of a stable emulsion at a shear rate of one reciprocal second, is at least three orders-of-magnitude greater than the fresh oil. An unstable emulsion usually has a viscosity no more than one order-of-magnitude greater than that of the starting oil. A stable emulsion has a significant elasticity, whereas an unstable emulsion does not. It should be noted that very few emulsions have questionable stability. Stable emulsions have sufficient asphaltenes ($>5\%$) to establish films of these compounds around water droplets.

Mesostable emulsions have insufficient asphaltenes to render them completely stable. Stability is achieved by viscoelastic retention of water and secondarily by the presence of asphaltene or resin films. Mesostable emulsions display apparent viscosities of about 80 to 600 times that of the starting oil and true viscosities of 20 to 200 times that of the starting oil.

A comparison of viscometer readings for characterizing emulsions was made. It was found that viscometers operating at high shear stress are not useful for emulsion characterization. Elasticity increases readings up to three-fold and the high shear rate breaks the emulsion and subsequently the viscosity readings fall through orders-of-magnitude within minutes.

1.0 Introduction

The most important characteristic of a water-in-oil emulsion is its "stability". The reason for this importance is that one must first characterize an emulsion as stable (or unstable) before one can characterize the properties. Properties change very significantly for each type of emulsion. (Until recently, emulsion stability has not been defined (Fingas *et al.* 1995b). Therefore, studies were difficult because the end points of analysis were not defined. The purpose of this paper will be to propose a definition of stability for water-in-oil emulsions and characteristics of different stability classes.

The 'stability' of an emulsion itself might be a question. Historically, emulsions were thought of as unstable, therefore any discussion of 'stability' would be considered trivial at best, and irrelevant at worst. This has changed in recent years.

Many commercial products resembling water-in-oil emulsions made from crude oil, have been shown to be stable, especially as it relates to their production, sale, storage and use as consumer products. A quick scan at the references in this paper shows that most workers in the field now discuss the 'stability' of water-in-oil emulsions.

It has been noted that the stability of emulsions can be grouped into three categories: stable, unstable and mesostable. These have been distinguished by physical properties. The viscosity of a stable emulsion at a shear rate of one reciprocal second, is at least three orders-of-magnitude greater than that of the starting oil. An unstable emulsion usually has a viscosity no more than two orders-of-magnitude greater than that of the starting oil. The zero-shear-rate viscosity for a stable emulsion is at least six orders-of-magnitude greater than that of the starting oil. For an unstable emulsion, it is usually less than two or three orders-of-magnitude greater than the viscosity of the starting oil. A stable emulsion has a significant elasticity, whereas an unstable emulsion does not. These properties can then be used in the design of any emulsion-breaking test as a quick analytical tool. Analytical techniques are then largely required to test the questionable emulsions or to rapidly confirm the stability of the others.

Studies in the past two years have shown that a class of 'very stable' emulsions exists, characterized by their persistence over several months. These stable emulsions actually undergo an increase in viscosity over time. Monitoring of these emulsions has been performed for over two weeks and new studies over much longer times are being conducted. 'Unstable' emulsions do not show this viscosity increase and their viscosity is less than two orders-of-magnitude greater than the starting oil. The viscosity increase for stable emulsions is at least three orders-of-magnitude greater than the starting oil. The present authors have studied emulsions for many years (Bobra *et al.* 1992; Fingas *et al.* 1993a, 1993b, 1993c, 1994a, 1994b, 1995a, 1995b). The last of these references describes studies to define stability. The findings of this study are summarized here. It was concluded both on the basis of the literature and experimental evidence above, that certain emulsions can be classed as stable. Some (if not all or many) stable emulsions increase in apparent viscosity with time (ie. their elasticity increases). The stability derives from the strong visco-elastic interface caused by asphaltenes, perhaps along with resins. Increasing viscosity may be caused by increasing alignment of asphaltenes at the oil-water interface.

Mesostable emulsions are emulsions that have properties between stable and unstable emulsions (really oil/water mixtures) (Fingas *et al.* 1995b). It is suspected that mesostable emulsions lack sufficient asphaltenes to render them completely stable or still contain too many de-stabilizing materials such as smaller aromatics. The viscosity of the oil may be high enough to stabilize some water droplets for a period of time. Mesostable emulsions may degrade to form layers of oil and stable emulsions. Mesostable emulsions can be red in appearance or black. Mesostable emulsions are probably the most commonly-formed emulsions in the field.

Unstable emulsions are those that decompose (largely) to water and oil rapidly after mixing, generally within a few hours. Some water may be retained by the oil, especially if the oil is viscous.

The most important measurements taken on emulsions are forced oscillation rheometry studies. The presence of elasticity clearly defines whether or not a stable emulsion has been formed. The viscosity by itself can be an indicator (not necessarily conclusive, unless one is fully certain of the starting oil viscosity) of the stability of the

emulsion. Colour is not a reliable indicator. This laboratory's experience is that all stable emulsions were reddish. Some mesoemulsions had a reddish colour and unstable emulsions were always the colour of the starting oil. Water content is not an indicator of stability and is error-prone because of 'excess' water that may be present.

2.0 Literature Review

In previous papers, the authors have reviewed the literature that relates to the formation and stability of emulsions (Fingas *et al.* 1995b; Fingas *et al.* 1996). The literature review here includes only that literature relevant to emulsion stability and formation published in the past year.

In 1996, a major monograph on emulsion stability was published, entitled "Emulsions and Emulsion Stability" (references in this document will be used throughout this paper). In chapter one of this book, Friberg and Yang review emulsion stability and de-stabilization processes (Friberg and Yang, 1996). The main processes of de-stabilization, flocculation, coalescence and creaming are described and mathematical descriptions of these processes given. Flocculation is usually the first process and consists of individual droplets approaching and becoming associated. This is distinguished from coalescence which is the combination of droplets. Creaming is the standard terminology for oil rising to the surface and forming a consistent surface layer.

Bibette and Leal-Calderon (1996) reviewed the stability of emulsions particularly as it relates to those which are surfactant-stabilized. They note that many of the processes are poorly understood, but that there is much more recent work in the field which promises to explain some of the physical processes.

Breen *et al.* (1996) reviewed emulsion stability. The source of stability for emulsions is the layer of asphaltenes (and resins) at the oil-water-interface. Several mathematical expressions for this stability are reviewed. Two forces stabilizing emulsions are confirmed, that of the surface-active forces and that of viscosity-based forces. The surface-active force, as created by the asphaltene layer, is the primary force responsible for long-term emulsion stability.

Dukhin and Sjöblom (1996) summarized the kinetics of emulsion coagulation. They noted that emulsion stability can be considered from four major viewpoints. Thermodynamic stability is usually thought of as being the primary criteria. Emulsions are not thermodynamically stable. Kinetic stability implies that emulsions are stable for a reasonable amount of time - eg. days. This is the definition of emulsion stability that is most operative. Aggregative stability implies stability by composition as a whole. If the aggregate retains its physical and chemical composition for the time under consideration, it can be considered to be stable.

Førdeedal *et al.* (1996a) studied crude oil emulsions in high electric fields. They found that the stability in water-in-oil (W/O) emulsions is due to the asphaltene fraction. They noted that although the resin fraction is surface-active, resins cannot, by themselves, stabilize an emulsion.

Førdeedal *et al.* (1996b) studied model crude oil emulsions by means of dielectric time-domain spectroscopy. Stability of the model emulsions varied with the choice of organic solvent and the amount of asphaltenes. Emulsions were less or not stable in aromatic solvents.

Førdeedal and Sjöblom (1996) studied percolation (a form of de-stabilization

phenomenon) in water-in-oil (W/O) emulsions. They noted that percolation did not occur readily for oils with high asphaltene contents and thus higher stabilities were attributed to emulsions.

Neumann and Paczynska-Lahme (1996) reviewed the stability and demulsification of W/O emulsions. Stability of emulsions is attributed to surface-active films consisting of several components, but primarily asphaltenes.

Puskas and co-workers (1996) studied water-in-oil emulsions and found that besides the usual stabilizers of asphaltenes and resins that a high-molecular weight paraffin was also capable of stabilizing water-in-oil emulsions. This paraffin had carbonyl functional groups and thus was polar and was found to exist in a colloid of lamellar structure.

Sjöblom and Førde (1996) reviewed the application of dielectric spectroscopy to emulsions. In this review, they consider the stability of water-in-oil emulsions. Asphaltenes at the interface are the source of stability for water-in-oil emulsions. It is noted that 2 to 3 % of asphaltenes are required to form stable emulsions. Resins are surface-active, but do not contribute strongly to emulsion stability.

The consensus of the literature is as follows:

1. stable and less-stable emulsions exist,
2. emulsion stability results from the viscoelastic films formed by asphaltenes,
3. asphaltenes produce more rigid films than do resins,
4. stable emulsions might be classified by their dielectric and viscoelastic properties,
5. water content does not appear to relate to stability, however, very low or very high water contents (<30 or >90%) will not yield stable emulsions,
6. most researchers use visible phase separation to classify emulsions as stable or not and most concede that this is not an optimal technique.

3.0 Experimental

Water-in-oil emulsions were made in a rotary agitator and then the rheometric characteristics of these emulsions studied over time. Three oils were used: Green Canyon, a Louisiana offshore oil, which is known to form unstable and mesostable emulsions; Arabian Light, which makes mesostable emulsions and Sockeye, a California oil, which makes stable emulsions (Fingas *et al.* 1995b, 1996). Data on oil properties are given in Table 1.

Table 1

Properties of the Fresh Test Oils

Parameter *	Arabian Light	Green Canyon	Sockeye
Density (15°C) g/mL	0.866	0.937	0.897
Viscosity (15°C) mPa.s	14	177	45
Complex Modulus mPa	200	1500	400
True Viscosity (15°C) mPa.s	20	200	40
Resins (wt. %)	6	14	13
Asphaltenes (wt. %)	3	4	8
Aromatics (wt. %)	39	40	31
Waxes (wt. %)	4	2	5
Total BTEX + C ₃ Benzenes (%)	1.5	0.33	1.5

* All values are taken from Jokuty et al. 1996 except for complex modulus and true viscosity, which were measured here.

Emulsions were made in a 8-place rotary agitator (Associated Design) which was equipped with a variable speed motor (1.5 to 56 rpm). The mixing vessels were Nalgene 2.2 litre wide mouth Teflon bottles. The fill was typically 500 mL salt water (3.3% w/v NaCl) and 25 mL oil. This yielded an oil-water-ratio of 1:20. Other ratios and fill volumes were used as noted in Table 2. Lower fill ratios yield higher energy levels and thus could influence the emulsion formation. Studies were performed always at 50 rpm, which was set using a tachometer.

Viscosities were characterized by several means. For characterization of apparent viscosity, the cup and spindle system was used. This consisted of the Haake Roto visco RV20 with M5 measuring system, Haake Rheocontroller RC20 and PC with dedicated software package Roto Visco 2.2. The sensors and vessels used were the SVI spindle and SV cup. The shear rate was one reciprocal second. The viscometer was operated with the following ramp times: one minute to target shear rate 1/s; one minute at target shear rate (1/s). The temperature was maintained at 15 degrees Celsius. Fifteen minutes was allowed for the sample to thermally equilibrate.

The following apparatuses were used for rheological analysis: Haake RS100 RheoStress rheometer, IBM-compatible PC with RS100-CS Ver. 1.28 Controlled Stress Software and RS100-OSC Ver. 1.1.4 Oscillation Software, 60 mm 4-degree cone with corresponding base plate, clean air supply at 40 p.s.i., and a circulation bath maintained at 15 degrees Celsius. Analysis was performed on a sample scooped onto the base plate and raised to the measuring cone. This was left for 15 minutes to thermally equilibrate at 15 degrees Celsius.

Controlled Stress was used for determining the linear viscoelastic range (stress independent region) and the creep and recovery analysis. The linear viscoelastic range (LVER) was determined first for all samples, as all measurements must be made in the LVER to be valid. It was determined by making a stress sweep over the stress range to identify the break point (estimates will speed this process). After identifying the stress independent range, two stress values were chosen for subsequent analysis - one close to the break point, and one other. These stress values were used in the oscillation procedures.

Forced Oscillation - this was used for determining the $\tan(\delta)$ (ratio of viscous to elastic components) zero-shear viscosity and G^* (total resistance to flow). Values were obtained from a stress sweep of the sample at 1 Hz. Calculation provides the final values.

Apparent Viscosity - For comparison purposes, a Brookfield Synchro-Lectric viscometer, model LVT, was employed with a L4 spindle. The unit was operated according to the instructions supplied by the manufacturer.

Water Content - A Metrohm 701 KF Titrino Karl-Fischer volumetric titrator and Metrohm 703 Ti Stand were used. The reagent was Aquastar Comp 5 and the solvent, 1:1:2 Methanol:Chloroform:Toluene.

4.0 Results and Discussion

The rheological data are given in Tables 2, 3 and 4. These tables provide the experimental variables as well as the results. The first line shows the fraction of the test vessel fill, generally $\frac{1}{2}$, but sometimes $\frac{1}{4}$. The less the fill, the more energy imparted to the oil and water. The ratio of oil to water is then given and this is 1:10, 1:20, 1:30, 1:40 or 1:50. The final value in the first line is the time of shaking which is 9 or 18 hours. The second line of the tables gives the complex modulus which is the vector sum of the viscosity and elasticity. The cone/plate viscosity is then given. The $\tan(\delta)$ is the ratio of the viscosity to the elasticity component. Then the end of the slope before the yield point (LVER) is given. The apparent viscosity from the RV-20 (Haake) is given and finally the water content of the emulsion.

Table 5 gives the results of viscosity measurements of the emulsions using the Brookfield viscometer, the plate-plate (RS100) viscometer and the Haake RV-20 viscometer. Further discussion on these results is given below.

Observations were made on the appearance of the emulsions. All of the Sockeye emulsions appeared to be stable and remained in tact over several days in the laboratory, except for those formed at the oil:water ratios of 1:50. All of the Arabian Light emulsions formed meso-stable emulsions and broke after a few days into water, free oil and emulsion. The time for these emulsions to break down varies from about 1 to 3 days. The emulsion portion of these break-down emulsions appears to be somewhat stable, although studies on them have not been performed. The Green Canyon emulsions were mesostable at formation ratios of 1:10 and 1:20 (O:W). These broke after about 1 day of sitting into water, oil and emulsion. Green Canyon emulsions formed at ratios of 1:30 (O:W) and higher were not stable and broke into water and oil within hours of mixing. It is suspected that the O:W ratio only relates to the shaking energy applied to the oil and may not be meaningful in itself.

The true viscosity of the emulsions is summarized in Table 6 and illustrated in Figure 1. These show that there exists a wide gap between the viscosities of stable

Table 2 Experimental Results for Green Canyon

Experimental Measurements *	units	Results After Specified Time									
		Immediate		1 day		1 week		1 month			
		Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
1/4 fill, 1:20, 9 hours											
Complex Modulus	mPa	72000	82000	56000	58000	50000	37500	41000	35000		
P/P Viscosity	mPa.s	9000	9300	8300	8600	8000	5800	6400	5500		
tan (delta)	viscous/elastic	1.1	1	2.1	2.3	4	3.5	5.4	8		
End of LVER	mPa	600	500	600	400	600	500	600	500		
RV20 Viscosity	mPa.s	14350	13300								
H ₂ O	%(w/w)	70.21	71.03	71.18	70.99	70.74	70.12	67.98	66.21		
1/2 fill, 1:20, 9 hours											
Complex Modulus	mPa	65000	75000	50000	70000	58000	52000	63000	48000		
P/P Viscosity	mPa.s	8000	8500	7000	9000	8800	7800	9600	7200		
tan (delta)	viscous/elastic	1.1	1.1	1.8	1.4	3.5	3	3	3		
End of LVER	mPa	700	400	600	400	600	1000	800	800		
RV20 Viscosity	mPa.s	14800	15400								
H ₂ O	%(w/w)	73.72	72.75	73.04	72.16	72.53	70.86				
1/4 fill, 1:20, 18 hours											
Complex Modulus	mPa	65000	35000	57000	58000	31000	35000				
P/P Viscosity	mPa.s	7500	5000	8000	8000	4000	5400				
tan (delta)	viscous/elastic	1	2.5	2	2	3	7				
End of LVER	mPa	700	200	300	200	200	100				
RV20 Viscosity	mPa.s	11600	11300								
H ₂ O	%(w/w)	70.13	69.64	69.42	68.35	69.99	70.24				
1/2 fill, 1:20, 18 hours											
Complex Modulus	mPa	52000	54000	37000	40000	30000	30000				
P/P Viscosity	mPa.s	7400	7500	5600	6100	4700	4700				
tan (delta)	viscous/elastic	1.9	1.6	3.9	3.2	5	6.9				
End of LVER	mPa	300	400	200	300	600	600				
RV20 Viscosity	mPa.s	13150	13750								

Table 2

Experimental Results for Green Canyon

Experimental Measurements *	units	Results After Specified Time							
		Immediate		1 day		1 week		1 month	
		Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
H ₂ O	% (w/w)	72.89	73.55	72.77	73.14	70.49	70.3		
1/4 fill, 1:10, 9 hours									
Complex Modulus	mPa	115000	120000	110000	105000	80000	66000		
P/P Viscosity	mPa.s	12000	12000	12000	11500	11000	10000		
tan (delta)	viscous/elastic	0.9	0.8	0.9	0.9	1.5	2		
End of LVER	mPa	400	400	500	500	700	800		
RV20 Viscosity	mPa.s	25200	24450						
H ₂ O	% (w/w)	77.32	76.87	76.33	77.31	74.47	75.91		
1/2 fill, 1:10, 9 hours									
Complex Modulus	mPa	105000	92000	76000	54000	53000	56000		
P/P Viscosity	mPa.s	11000	9700	10000	8000	7800	8200		
tan (delta)	viscous/elastic	0.85	0.9	1.2	2.2	2.5	2.5		
End of LVER	mPa	400	700	500	600	500	300		
RV20 Viscosity	mPa.s								
H ₂ O	% (w/w)	77.08	78.46	76.89	76.93	73.87	74.39		
1/2 fill, 1:50, 9 hours									
Complex Modulus	mPa	4200							
P/P Viscosity	mPa.s	640							
tan (delta)	viscous/elastic	3.2							
End of LVER	mPa	no break							
RV20 Viscosity	mPa.s	Unable to measure due to quantities							
H ₂ O	% (w/w)	34.66	25.36						
1/2 fill, 1:30, 9 hours									
Complex Modulus	mPa	1300	11800	18500	13400	37500	31500		
P/P Viscosity	mPa.s	2000	1850	2800	2000	5600	4800		
tan (delta)	viscous/elastic	5.8	6	3.5	2.5	2.3	3		

Table 2 Experimental Results for Green Canyon

Experimental Measurements *	units	Results After Specified Time									
		Immediate		1 day		1 week		1 month			
		Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
End of LVER	mPa	600	500	400	500	1500	1000				
RV20 Viscosity	mPa.s	6550	6400								
H ₂ O	% (w/w)	65.59	57.26	58.15	60.05						
1/2 fill, 1:40, 9 hours											
Complex Modulus	mPa	4500	4000	7000	7200	42000	45000				
P/P Viscosity	mPa.s	700	600	1100	1100	6500	6800				
tan (delta)	viscous/elastic	10	20	20	10	4	3				
End of LVER	mPa	no break	no break	no break	no break	2000	1500				
RV20 Viscosity	mPa.s	5050	4900								
H ₂ O	% (w/w)	44.72	37.73	33.38	35.4						

Typical Green Canyon 65 emulsion turns red/brown, but does not become semi-solid after sitting.

* see text for full explanation of this column; first line summarizes shaking experiments, others measurements

Table 3
Experimental Results for Arabian Light

Experimental Measurements *	units	Results After Specified Time									
		Immediate		1 day		1 week		1 month			
		Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
1/4 fill, 1:20, 9 hours											
Complex Modulus	mPa	148000	105	31000	29500	21000	23000	19500	20000		
P/P Viscosity	mPa.s	4800	4100	2200	1900	1550	1500	1650	1550		
tan (delta)	viscous/elastic	0.2	0.2	0.5	0.4	0.5	0.5	0.5	0.6		
End of LVER	mPa	100	500	60	80	80	50	50	50		
RV20 Viscosity	mPa.s	14300	12900								
H ₂ O	%(w/w)	81.46	84.15	75.77	76.05	79.14	82.45				
1/2 fill, 1:20, 9 hours											
Complex Modulus	mPa	60000	78000	24000	33000	38000	29000	76000	60000		
P/P Viscosity	mPa.s	2800	3500	1800	2000	2300	2300	4100	4000		
tan (delta)	viscous/elastic	0.3	0.3	0.55	0.6	0.4	0.45	0.35	0.45		
End of LVER	mPa	500	200	60	50	50	150	90	100		
RV20 Viscosity	mPa.s	8000	9200								
H ₂ O	%(w/w)	79.63	80.12	81.12	83.78	85.77	87.22				
1/4 fill, 1:20, 18 hours											
Complex Modulus	mPa	150000	250000	55000	28000	100000	90000				
P/P Viscosity	mPa.s	5400	7500	3500	2300	4500	4200				
tan (delta)	viscous/elastic	0.25	0.2	0.4	0.6	0.3	0.3				
End of LVER	mPa	200	100	100	70	150	300				
RV20 Viscosity	mPa.s	16000	14750								
H ₂ O	%(w/w)	85.59	85.02	82.53	84.06	86.88	86.81				
1/2 fill, 1:20, 18 hours											
Complex Modulus	mPa	120000	80000	115000	34000	65000	82000				
P/P Viscosity	mPa.s	4500	3900	4700	2550	2900	3850				
tan (delta)	viscous/elastic	0.23	0.28	0.25	0.52	0.27	0.3				
End of LVER	mPa	200	400	600	60	400	200				
RV20 Viscosity	mPa.s	10350	11450								
H ₂ O	%(w/w)	84.25	82.98	82.56	77.67	87.44	84.23				
1/4 fill, 1:10, 9 hours											
Complex Modulus	mPa	140000	70000	8000	11000	125000	72000				
P/P Viscosity	mPa.s	5700	4200	720	900	5400	3800				
tan (delta)	viscous/elastic	0.26	0.38	0.7	0.6	0.26	0.33				
End of LVER	mPa	200	500	60	150	150	500				
RV20 Viscosity	mPa.s	11400	8950								
H ₂ O	%(w/w)	84.34	85.1	88.82	87.72	86.87	84.93				

Table 3 Experimental Results for Arabian Light

Experimental Measurements *	units	Results After Specified Time									
		Immediate		1 day		1 week		1 month			
		Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2		
		Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2		
1/2 fill, 1:10, 9 hours											
Complex Modulus	mPa	57000	38000	7000	3600	32000	45000				
P/P Viscosity	mPa.s	3200	2700	700	380	2000	2600				
tan (delta)	viscous/elastic	0.4	0.4	0.8	0.9	0.4	0.4				
End of LVER	mPa	150	600	70	50	150	100				
RV20 Viscosity	mPa.s										
H ₂ O	% (w/w)	90.03	90.21	75.56	79.33	83.04	82.02				
1/2 fill, 1:50, 9 hours											
Complex Modulus	mPa	4300	5000								
P/P Viscosity	mPa.s	3100	3500								
tan (delta)	viscous/elastic	0.5	0.4								
End of LVER	mPa	200	500								
RV20 Viscosity	mPa.s	7250	8150								
H ₂ O	% (w/w)	87.55	86.42								
1/2 fill, 1:30, 9 hours											
Complex Modulus	mPa	130000	98000	34000	45000	44000					
P/P Viscosity	mPa.s	4200	4000	2300	2400	2700					
tan (delta)	viscous/elastic	0.2	0.23	0.45	0.35	0.4					
End of LVER	mPa	200	1500	200	200	150					
RV20 Viscosity	mPa.s	12850	11650								
H ₂ O	% (w/w)	84.73	86.6	84.62	84.73	85.02					
1/2 fill, 1:40, 9 hours											
Complex Modulus	mPa	65000	70000	53000	45000	30000	32000				
P/P Viscosity	mPa.s	3800	3500	3000	2700	2200	2500				
tan (delta)	viscous/elastic	0.4	0.3	0.4	0.4	0.5	0.55				
End of LVER	mPa	200	1000	500	200	300	70				
RV20 Viscosity	mPa.s	12300	12700								
H ₂ O	% (w/w)	83.74	83.72	86.52	85.96						

Arabian light oil emulsions would typically form emulsions with large droplets and these would separate after a period of time

* see text for full explanation of this column; first line summarizes shaking experiments, others measurements

Table 4
Experimental Results for Sockeye

Experimental Measurements *	units	Results After Specified Time									
		Immediate		1 day		1 week		1 month			
		Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
1/4 fill, 1:20, 9 hours											
Complex Modulus	mPa	780000	530000	500000	450000	550000	450000	530000	380000		
P/P Viscosity	mPa.s	27000	19500	21400	18300	23500	19200	23000	18000		
tan (delta)	viscous/elastic	0.2	0.25	0.25	0.25	0.25	0.28	0.25	0.3		
End of LVER	mPa	2000	2000	8000	2500	1000	2500	1000	2500		
RV20 Viscosity	mPa.s	104200	102800								
H ₂ O	%(w/w)	84.48	84.83	84.14	84.84	81.92	82.35				
1/2 fill, 1:20, 9 hours											
Complex Modulus	mPa	960000	1000000	950000	820000	700000	650000	630000	600000		
P/P Viscosity	mPa.s	27500	27500	30000	27500	65000	25500	27000	27000		
tan (delta)	viscous/elastic	0.2	0.2	0.2	0.2	0.25	0.25	0.3	0.3		
End of LVER	mPa	6000	3000	6000	7000	6000	6000	4000	4000		
RV20 Viscosity	mPa.s	168200	171400								
H ₂ O	%(w/w)	88.14	86.33	85.48	86.81	84.74	83.83				
1/4 fill, 1:20, 18 hours											
Complex Modulus	mPa	980000	950000	920000	800000	700000	680000	700000	700000		
P/P Viscosity	mPa.s	34000	33000	36000	31600	29000	28000	25000	29000		
tan (delta)	viscous/elastic	0.2	0.25	0.25	0.25	0.3	0.3	0.3	0.3		
End of LVER	mPa	2000	1500	6000	1500	5000	8000	2000	2000		
RV20 Viscosity	mPa.s	152800	123400								
H ₂ O	%(w/w)	85.19	84.99	83.19	83.58	82.52	84.48				
1/2 fill, 1:20, 18 hours											
Complex Modulus	mPa	1050000	1250000	980000	1180000	750000	850000				
P/P Viscosity	mPa.s	34000	38000	34000	38000	29500	32000				
tan (delta)	viscous/elastic	0.2	0.19	0.21	0.21	0.25	0.24				
End of LVER	mPa	8000	10000	8000	7000	9000	10000				
RV20 Viscosity	mPa.s	223900	218000								
H ₂ O	%(w/w)	87.66	87.52	87.66	87.52	83.89	84.17				
1/4 fill, 1:10, 9 hours											
Complex Modulus	mPa	330000	320000	180000	170000	180000	165000				
P/P Viscosity	mPa.s	11200	10500	6700	6500	6700	7000				
tan (delta)	viscous/elastic	0.25	0.2	0.3	0.3	0.2	0.1				
End of LVER	mPa	600	300	10000	10000	10000	10000				
RV20 Viscosity	mPa.s	67600	73300								
H ₂ O	%(w/w)	91.8	91.91	89.51	88.81	84.68	83.09				

Table 4
Experimental Results for Sockeye

Experimental Measurements *	units	Results After Specified Time									
		Immediate		1 day		1 week		1 month		Sample 1	Sample 2
		Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2		
1/2 fill, 1:10, 9 hours											
Complex Modulus	mPa	200000	200000	160000	190000	160000	200000	200000	200000		
P/P Viscosity	mPa.s	8000	7500	6300	7000	6400	7800	7800	7800		
tan (delta)	viscous/elastic	0.1	0.2	0.2	0.3	0.1	0.3	0.1	0.3		
End of LVER	mPa	10000	10000	10000	12000	10000	20000	20000	20000		
RV20 Viscosity	mPa.s										
H ₂ O	% (w/w)	88.77	90.07	90.84	91.15	84.77	85.39	84.77	85.39		
1/2 fill, 1:50, 9 hours											
Complex Modulus	mPa	760000	820000								
P/P Viscosity	mPa.s	2500	2800								
tan (delta)	viscous/elastic	0.2	0.23								
End of LVER	mPa	9000	2000								
RV20 Viscosity	mPa.s	136300	129600								
H ₂ O	% (w/w)	85.23	86.03								
1/2 fill, 1:30, 9 hours											
Complex Modulus	mPa	750000	640000	550000	580000	480000	580000	580000	580000		
P/P Viscosity	mPa.s	24000	22000	21000	21000	20000	23000	23000	23000		
tan (delta)	viscous/elastic	0.22	0.22	0.24	0.24	0.25	0.25	0.25	0.25		
End of LVER	mPa	2000	5000	8000	4000	2000	1500	2000	1500		
RV20 Viscosity	mPa.s	131700	132500								
H ₂ O	% (w/w)	84.24	85.86	83.2	82.18						
1/2 fill, 1:40, 9 hours											
Complex Modulus	mPa	650000	640000	670000	630000	700000	630000	630000	630000		
P/P Viscosity	mPa.s	24000	22000	26000	22000	26000	25000	25000	25000		
tan (delta)	viscous/elastic	0.2	0.23	0.25	0.25	0.25	0.25	0.25	0.25		
End of LVER	mPa	8000	6000	8000	7000	10000	8000	10000	8000		
RV20 Viscosity	mPa.s	119600	107500								
H ₂ O	% (w/w)	83.85	83.86	82.18	82.52						

Typical emulsion was red/brown and viscous, and breaks in chunks (semi-solid) after sitting for a period of time.
* see text for full explanation of this column; first line summarizes shaking experiments, others measurements

Table 5 Comparison of Viscosity Measurements

Oil	Sample #	Time (min)	RPM LV4 spindle	Brookfield Viscosity (mPa.s)	RS100 Viscosity (mPa.s)	RV20 Viscosity (mPa.s)
Arabian Light	0303-3	1	60	< 500	4500	10350
		5	60	< 500		
		10	60	< 500		
		15	60	< 500		
(LV2 spindle)	0303-4	1	0.6	13500	3900	11450
		5	0.6	13000		
		10	0.6	13000		
		15	0.6	13000		
Green Canyon 65	0220-2	1	30	3600	9300	13300
		5	30	3600		
		10	30	3600		
		15	30	3600		
	0303-1	1	60	2200	7400	13150
		5	60	2100		
		10	60	2200		
		15	60	2400		
	0303-2	1	30	2200	7500	13750
		5	30	2400		
		10	30	2800		
		15	30	3000		
	0304-1	1	30	6200	12000	25200
		5	30	7000		
		10	30	6800		
		15	30	6400		
	0304-2	1	30	5600	12000	24450
		5	30	6600		
		10	30	5600		
		15	30	5600		
	0306-1	1	30	3000	11000	
		5	30	3200		
		10	30	3600		
		15	30	3600		
	0306-2	1	30	3000	9700	
		5	30	3400		
		10	30	3800		
		15	30	4000		
Sockeye	0303-5	1	0.6	560000	34000	223900
		5	0.6	400000		
		10	0.6	340000		
		15	0.6	290000		
	0303-6	1	0.6	540000	38000	218000
		5	0.6	430000		
		10	0.6	320000		
		15	0.6	280000		
	0304-5	1	1.5	76000	11200	67600
		5	1.5	52000		
		10	1.5	48000		
		15	1.5	44000		
	0304-6	1	1.5	64000	10500	73300
		5	1.5	52000		
		10	1.5	48000		
		15	1.5	44000		
	0306-5	1	1.5	100000	8000	
		5	1.5	64000		
		10	1.5	56000		
		15	1.5	52000		
	0306-6	1	1.5	88000	7500	
		5	1.5	64000		
		10	1.5	64000		
		15	1.5	60000		
	0313-5	1	0.6	440000	25000	136300
		5	0.6	350000		
		10	0.6	270000		
		15	0.6	250000		
	0313-6	1	0.6	470000	28000	129600
		5	0.6	350000		
		10	0.6	280000		
		15	0.6	240000		

and mesostable emulsions and a lesser, but discernable, gap between the mesostable and unstable emulsions. Table 7 shows the differences between the starting oil and the emulsion viscosities (true rather than apparent values). These are illustrated in Figure 2. These tables show that the stable emulsion has a viscosity about 700 times that of the starting fresh oil, the mesostable from 40 to 200 times the starting oil and the unstable, values less than 40. This can be compared with the apparent viscosities (those viscosity measurements which include elasticity), given in Table 8, where the stable Sockeye emulsion has a viscosity about 3000 times that of the starting oil. The mesostable emulsions have apparent viscosities about 80 to 600 times that of the starting oil.

The effect of the formation ratios was noted. This is summarized in Table 9. It should be noted that the effect of the ratios also affects the energy levels in the shaker. Thus conclusions about this are difficult to draw.

Three different types of viscometers were used to perform the measurements. The RS100 is a stress-controlled rheometer which provides true viscosity measurements along with other rheometric parameters. The RV20 is an advanced cup and spindle instrument, with variable shear control, which provides an apparent viscosity measurement. The Brookfield is a smaller unit which has no shear stress control. The summary of the difference between results is shown in Table 10. This is illustrated in Figure 3. As can be seen by these values, a high shear instrument such as the Brookfield results in erroneous values, especially after time. Some of the time and viscosity relationships are illustrated in Figure 4. This shows that viscosities changes by orders-of-magnitude over a few minutes. Figure 3 shows that the 95% confidence level for the Brookfield is very wide, even if one only uses the 1 minute viscosity value. The errors for the Brookfield are too high to use as a reliable measurement instrument for an unknown emulsion. The high elasticity of emulsions, which is read by non-shear stress-controlled instruments, leads to very high initial viscosity readings - as much as a factor of 3 over the true value. The high shear of the instrument 'breaks' the emulsion over time and soon a much lower reading is given. This is unpredictable and depends on several characteristics of the emulsion. Therefore, the Brookfield reading is almost a random one unless used with a known substance under very controlled conditions.

The relationship of these data to the field is of relevance. The laboratory experience is that meso-stable emulsions would not separate under continuous agitation as would be experienced at sea, however, any free oil separating would form a slick which could move away from the emulsion. Another scenario is that under energetic conditions, high sea energies could maintain an emulsion simply because the injection of water droplets could equal that lost by separation. Upon cessation of the high energy, the 'emulsion' would separate. Both scenarios could explain some of the observations at several spill sites.

The role of asphaltenes in the emulsion formation appears again in these three oils. The most stable emulsion was produced by Sockeye which had the highest asphaltene content, 8%. All of these oils had high resin contents, again indicating that asphaltenes are more responsible for high stabilities.

Table 6 Summary of True Viscosity Differences for Emulsions

Emulsion type	Average Viscosity of Emulsion Samples (mPa.s)				
	days	0	1	7	30
stable, Sockeye		27700	27200	28900	24900
mesostable, Arabian Light		4100	2100	2900	2800
mesostable, Green Canyon		8900	8500	7200	7200
unstable, Green Canyon		1100	1800		
Emulsion type	Standard Deviation of above Data (mPa.s)				
	days	0	1	7	30
stable, Sockeye		5400	6100	1110	3300
mesostable, Arabian Light		1200	1200	1100	1400
mesostable, Green Canyon		2100	1900	2200	1800
unstable, Green Canyon		700	800		

Table 7 Summary of Differences between Emulsion and Starting Oil Viscosity

Emulsion type	Ratio of Viscosity of Emulsion and Starting Oil				
	days	0	1	7	30
stable, Sockeye		690	680	720	620
mesostable, Arabian Light		210	110	150	140
mesostable, Green Canyon		40	40	40	40
unstable, Green Canyon		10	10		

Table 8 Apparent Viscosity Differences Between Emulsions and Starting Oil

Emulsion type	Apparent Viscosity at formation mPa.s	Standard Deviation mPa.s	Ratio to Starting Oil	Ratio to True Viscosity
	mPa.s	mPa.s	Oil	Viscosity
stable, sockeye	152900	42800	3820	6
mesostable, Arabian Light	11800	2500	590	3
mesostable, Green Canyon	15700	1500	80	2
unstable, Green Canyon	5700	900	30	5

Table 9 Effect of Formation Oil:Water Ratio on Stability

O:W Ratio and Type	Days	0	1	7	30
1:10 Sockeye, mesostable	9300	6600	7000		
1:20 Sockeye, stable	30100	29500	31500		24800
1:30 Sockeye, stable	23000	21000	21500		
1:40 Sockeye, stable	23000	24000	25500		
1:50 Sockeye, unstable	2700				
no significant difference for Arabian Light					
All Arabian Light -mesostabl	4100	2100	2900		2800
1:10 Green Can. mesostable	11200	10400	9300		
1:20 Green Can. mesostable	8900	8500	7200		
1:30 Green Can. unstable	1900	2400	5200		
1:40 Green Can. unstable	700	1100	6700		
1:50 Green Can. unstable	600				

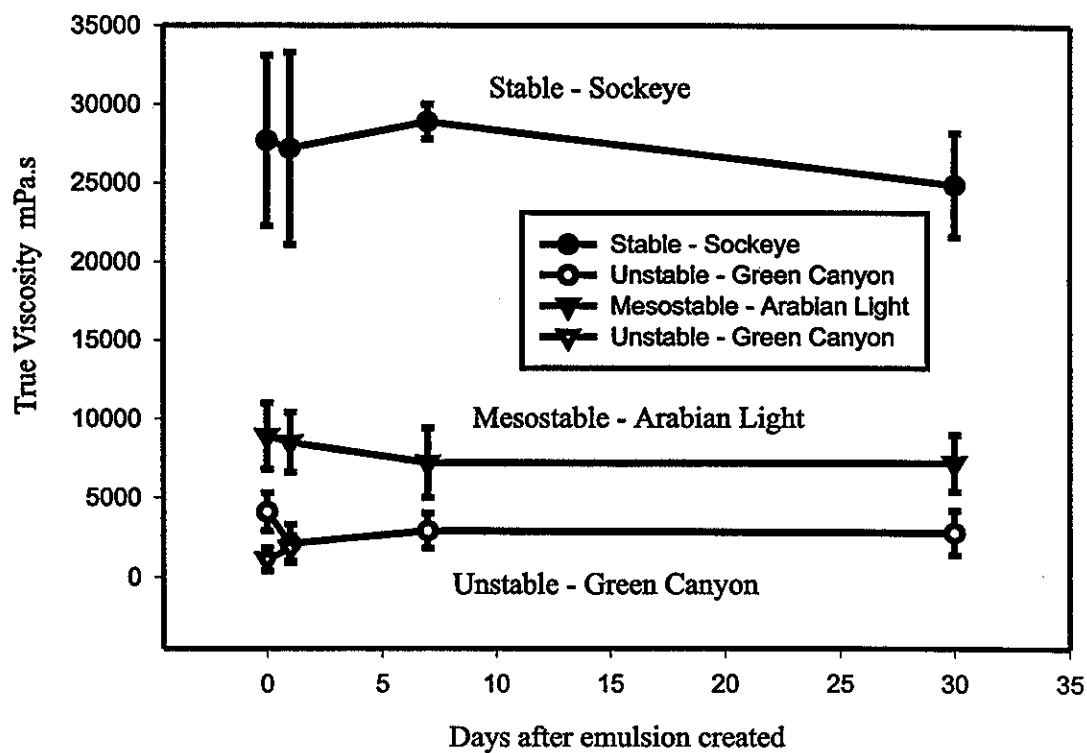


Figure 1 Viscosity of Emulsions over Time

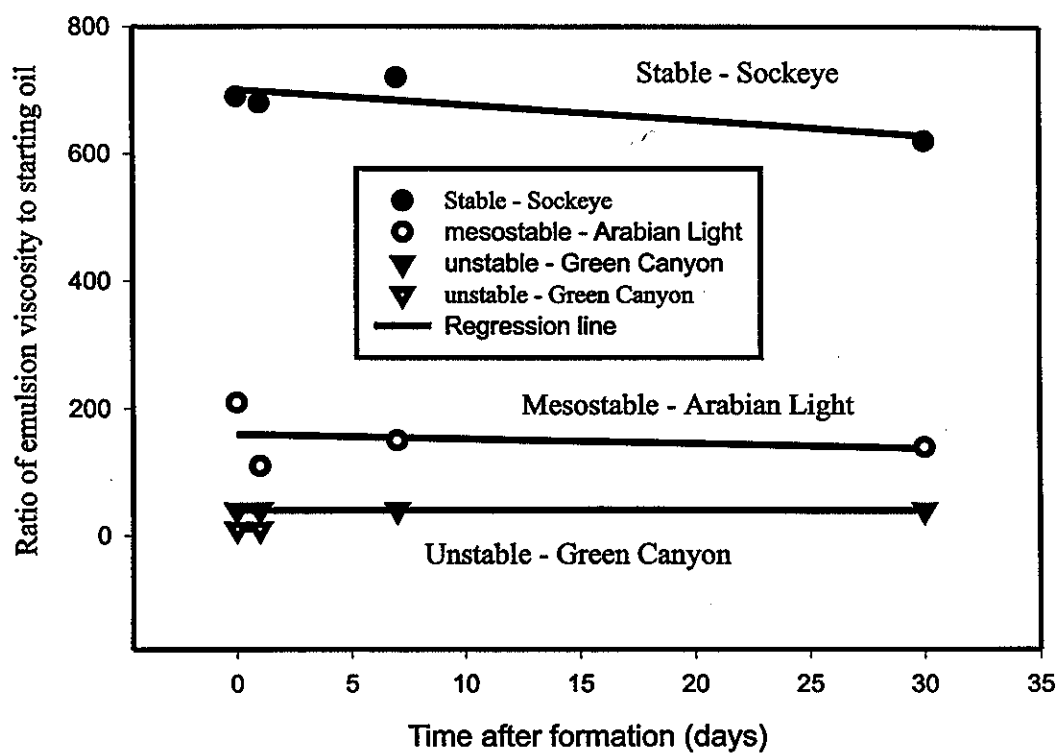


Figure 2 Ratios of True Viscosities of Emulsion to Starting Oil

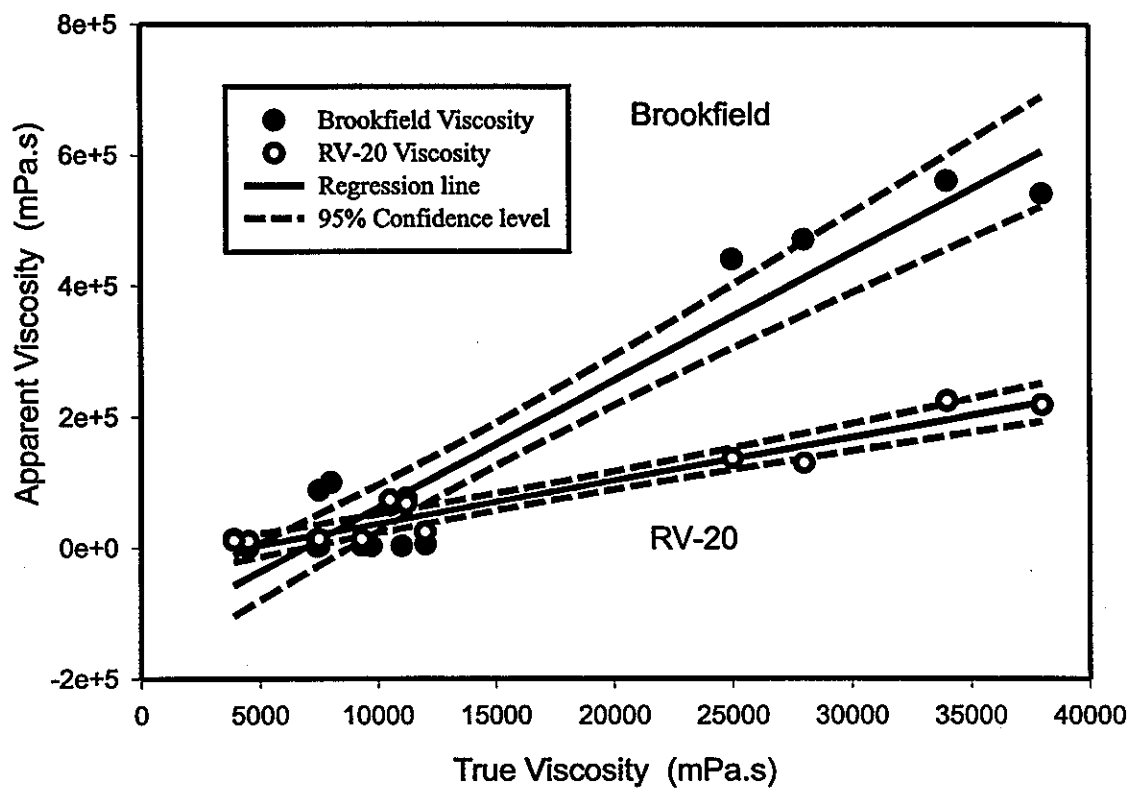


Figure 3 Comparison of Viscosity Measurements

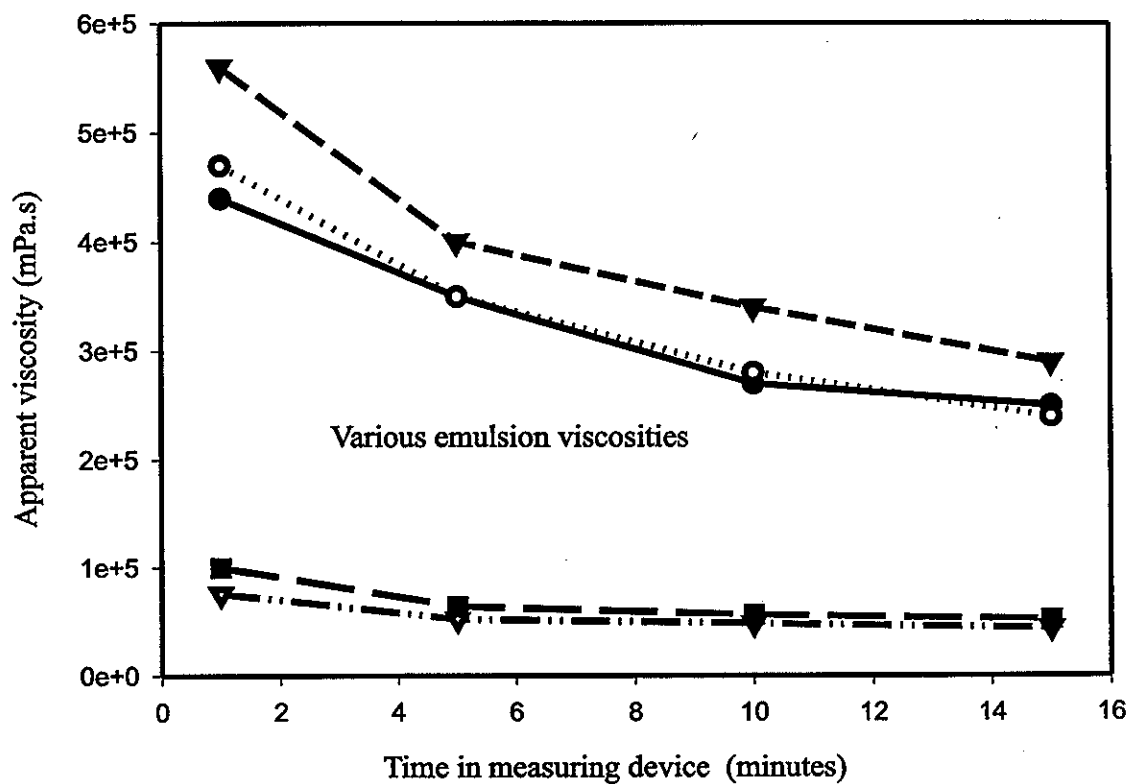


Figure 4 Change of Viscosity with Time in Brookfield Viscometer

Table 10 Summary Comparison of Viscosity Measurements

Oil	Sample #	RPM LV4 spindle	Apparent Viscosity	True Viscosity	Apparent Viscosity
			Brookfield Viscosity (mPa.s)	RS100 Viscosity (mPa.s)	RV20 Viscosity (mPa.s)
Arabian Light (LV2 spindle)	0303-3	60	<500	4500	10350
	0303-4	0.6	13500	3900	11450
Green Canyon 65	0220-2	30	3600	9300	13300
	0303-1	60	2200	7400	13150
	0303-2	30	2200	7500	13750
	0304-1	30	6200	12000	25200
	0304-2	30	5600	12000	24450
	0306-1	30	3000	11000	
	0306-2	30	3000	9700	
	0303-5	0.6	560000	34000	223900
Sockeye	0303-6	0.6	540000	38000	218000
	0304-5	1.5	76000	11200	67600
	0304-6	1.5	64000	10500	73300
	0306-5	1.5	100000	8000	
	0306-6	1.5	88000	7500	
	0313-5	0.6	440000	25000	136300
	0313-6	0.6	470000	28000	129600

5.0 Conclusions

The rheometric studies on the emulsions of three oils shows that there exist large differences in the viscosities (both apparent and true) of unstable, mesostable and stable emulsions. The results are summarized in Table 10.

Table 11 Summary of Emulsion Characteristics

Parameter	Mesostable Emulsion	Stable Emulsion
True viscosity difference from starting oil	20-200	700
Apparent viscosity difference from starting oil	80-600	3000
Lifetime	< 3 days	infinite
Appearance before breaking	viscous brown mass	solid-like brown mass
Appearance after breaking	3-layers	not relevant
Main stabilizing force	viscoelasticity	asphaltene film
Secondary stabilizing force	asphaltene film	viscoelasticity

The studies show that there are some variations in the formation of emulsions relating to the energy of formation. These require further investigation.

The comparison of measurement techniques shows that viscometers which do not apply controlled stress are not accurate for characterizing unknown emulsions.

Elasticity produces high viscosity readings and the high shear stress rate can break some emulsions producing unusually low readings. The latter occurs over time and thus the readings are highly time dependent.

The results presented in this paper are consistent with previous results from the present authors and the literature. It was suggested that mesostable emulsions lack sufficient asphaltenes to render them completely stable or still contain too many destabilizing materials such as smaller aromatics. The viscosity of the oil may be high enough to stabilize some water droplets for a period of time. Mesostable emulsions are probably the most commonly-formed emulsions in the field. It was noted that stable emulsions derive from oils that have asphaltene contents greater than 3 to 5% and a lower (as yet undefined) aromatic content. It was suspected that the BTEX content was most important because these can dissolve the asphaltenes. Further work on the interaction of these components is necessary before exact prediction of emulsion formation can occur.

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